

EFFECT OF TiO_2 ON CRYSTALLIZATION AND MECHANICAL PROPERTIES OF BLAST FURNACE (BF) SLAG BASED GLASS CERAMICS

*A Thesis submitted to
National Institute of Technology, Rourkela
For the award of the degree*

of

**Master of Technology
In
Industrial Ceramics**

by

**Sandeep Kumar
Roll No.: 213CR2131**



**DEPARTMENT OF CERAMIC ENGINEERING
NATIONAL INSTITUTE OF TECHNOLOGY, ROURKELA**

May-2015

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Under the supervision of
Prof. Arun Chowdhury



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May-2015**



DEPARTMENT OF CERAMIC ENGINEERING
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CERTIFICATE

This is to verify that the thesis titled *“Effect of TiO_2 on crystallization and mechanical properties of Blast Furnace (BF) slag based Glass ceramics”*, submitted to the National Institute of Technology, Rourkela by **Mr. Sandeep Kumar**, Roll No. **213CR2131** for the award of Master of Technology in Ceramic Engineering, is a bona fide record of research work carried out by him under my supervision and guidance.

The candidate has fulfilled all the prescribed requirements.

The Thesis, which is based on candidate's own work has not submitted elsewhere for a degree/diploma.

In my opinion, the thesis is of standard required for the award of a Master of Technology degree in Ceramic Engineering.

Arun Chowdhury

Prof. Arun Chowdhury

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213CR2131

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Abstract

Glass ceramics has an extensive variety of uses in today's reality. The generation of glass ceramics production from mechanical waste, for example, fly ash, red mud, blast furnace slag increasing more significance now a day's due to their accessibility and minimal effort. Accordingly utilizing blast furnace slag as one of the primary constituents can help in decreasing the liquefying temperature of the precursor glass prior to glass ceramic production. In the present work, an endeavor has been made to deliver glass ceramic with high TiO_2 substance utilizing blast furnace slag. A new glass-ceramic was created from an extra TiO_2 -containing Blast furnace slag. The high amount of TiO_2 (5-10 wt%) in this system shifting oxide and increases crystallization in the glass system, bringing about a superior-grained material which have good mechanical properties. Glass batches are dissolved at 1450°C . Glass ceramization treatment temperatures were chosen 800°C , 900°C , 1000°C and 1100°C . Glass Ceramic products are characterize by Vickers Hardness, Bulk density measurement, Flexural strength , Compressive strength , Dilatometer test, X-ray Diffraction (XRD) , Differential Scanning Calorimetry (DSC) and Field-emission Scanning Electron Microscopy (FESEM). The crystallization level was examined with the density variation with temperature. A higher density was found at 900°C . A striking difference in the composition of glass-ceramic was observed by heat treating the glass at different crystallization temperatures. Diopside and Gehlenite were found as major phases with the help of XRD. A high micro-hardness of 7 GPa, Bulk density above 3gm/cc and a Compressive strength greater than 100 MPa were found. The resultant glass ceramic is high-quality, tastefully worthy (metallic dark or misty cocoa shaded), and suitable for structural and building application.

CHAPTER: 1

INTRODUCTION

Introduction

Blast furnace slag is a major waste delivered by iron and steel industry. It is likewise profitable asset for reusing and utilizing. The Blast furnace slag is generally quenched from 1450°C, and therefore utilized as crude materials for concrete and solid, which normally has the minor amount. Because of these methodologies air, water and dust discharge contaminations coming out [1]. Environment and human wellbeing impacts are unpredictably connected, in this way the requirement for waste reusing is good for healthy life today. Researchers and technologists are seeking approaches to decrease the natural effect of wastes that is disposed of in landfills and upgrade the security of nature from vaporous and dust emissions also. It is the fact that it is economically important for industries for advancement and brings out a good and healthy life for lots of workers in the world and understanding their need. Air and water pollution is not only fact also land filling disposals are the responsible for the environmental pollution [2].

Discovering utilization of different slag is a critical issue for industries in both financial and economical perspective. A huge number of huge amounts of slag are delivered the world over, so its transfer in unique dumpsites is excessive, and it is not an economical arrangement, [4, 10]. As development materials, the mechanical and thermal properties of glass–ceramics are better than marble. Glass–ceramics additionally shows some other amazing properties which are valuable for specific fields, such as higher strength, better thermal shock resistance, and low expansion.

The Blast furnace slag is framed in the methods of pig iron made from iron metal. It contains combustion deposit of coke, fluxes of limestone and other different materials. In the incident when the liquid slag cools down rapidly by water quenching method, Ca–Al–Mg–Si fine grain glassy type material formed. It reveals that the blast furnace slag can be used as a glass source for developing the glass ceramics and waste disposals can be avoided. The free surface of glass is ideal for devitrification and in this way crystallization may be easily occurring in the glass without any use of other nucleating agents. Along these lines, after converting slag in fine powder form it can be utilized for the formation of glass [5]. These slags generally have main composition CaO , SiO_2 , Al_2O_3 and MgO with some minor impurities, for example, MnO , Fe_2O_3 and S . As a recycling material blast furnace slag was the first silicate waste that used for developing as the glass

ceramics. In now a days some other silicate wastes like fly ash, red mud is also using for the development of some other new glass ceramics [10].

Glass ceramic is the material that first framed as glass material and after this converted into a new crystalline material by reheating at a certain temperature. Generally crystallization and glassy nature of these materials depends on some factors like crystallization temperature, heat treatment time and the amount of nucleating agents. The exploration exercises and endeavors did by a few creators in the field of other wastes utilization in making of some other useful glass ceramics is also useful for economical and ecological system. It is concluded by examine different properties that the glass ceramics developed with the silicate wastes like blast furnace slag are useful for storage of grating materials as tiles and funnels because glass-ceramic materials are significantly much better than metals and alloys [2].

It is conceivable to plan glass ceramic production from metallurgical slag. A few aftereffects of planning glass ceramic from different slags have been presented by different researchers. Francis inquired about on the blast furnace slag derived glass ceramic and found different crystalline phases named diopside pyroxene, gehlenite, and barium aluminum silicate. Khater directed an examination concerning the glass ceramic from Saudi slag and observed the diopside crystalline phase at around 1120°C. Wang and Liang did research on glass ceramic developed from titanium slag and fly ash. Furthermore, it is no doubt understood that glass ceramics developed from different types of slags generally have great mechanical properties and in addition substance properties. Subsequently, the innovation to reuse metallurgical slag is discriminatingly essential to secure the earth as well as to give helpful material [3].

In the glass-ceramic framework the nucleating operators, for example, CaF_2 , TiO_2 were utilized as a part of the request to actuate mass crystallization in the phases and to lower the maximum crystallization temperature. It is additionally realized that glass composition contains from 2 to 20 wt% TiO_2 take form with the development of identical fine-grained microstructures. The ideal measure of TiO_2 is subject to the glass composition and increments with diminishing SiO_2 content. Be that as it may, the existence of TiO_2 is greater than 20wt% can prompt the precipitation of TiO_2 crystals and a decline in the nucleation and development of the desired crystalline phase.

Generally, a nucleating substance is mixed in the glass-ceramic composition for more nucleation of crystals inside the glass matrix to happen productively, bringing about countless or nano-sized crystals. Be that as it may, from the characteristic more amount of TiO_2 in the glass, resultant glass ceramic have greater strength and other mechanical properties in comparison to that glass ceramics which have no extra nucleating agent.

The essential point of the present study is to focus a minimal effort approach to get low-cost Blast furnace derived glass ceramics, with the structure and crystallization plan. The crystallization conduct of the glass and the impact of TiO_2 on its microstructure during the methodology are likewise examined by differential filtering calorimetry (DSC), Field emission scanning electron microscope (FESEM) and X-ray diffraction analysis (XRD).

1.1 Objective and scope:

- Recycling and utilizing of silicate wastes as a raw material for the development of glass ceramics.
- Development of Blast furnace slag based glass-ceramics with nucleating agent TiO_2 . Study the effect of TiO_2 as a nucleating agent in the Blast furnace slag based glass-ceramics.
- Improving mechanical properties of glass ceramic after controlled nucleation and crystal growth in glass-ceramics for structural and architectural applications.

CHAPTER: 2

LITERATURE REVIEW

Literature Review

Zhao et.al [1] studied the preparation of low-cost glass–ceramics from molten blast furnace slag and concluded the following. The usage proportion of blast furnace slag was dependent upon around 90 wt%, which guaranteed less raw materials cost. The main crystalline phases determined akermanite and diopside. The flexural strength of the specimen came to 45.8 MPa. The strength of glass–ceramics specimen were likewise enhanced, up to 120 MPa when 7.6% CaF_2 was included.

Francis [2] studied the utilization of blast furnace slag for making a new glass ceramic material. Blast furnace slag can effectively converted into new glass ceramic material. The experiments were successful to convert blast furnace slag into a valuable item. The rapid and sharp crystallization with increasing the heating rate shows that the mass crystallization is predominant in the glass ceramic. The level of crystallization was controlled by assessment the progressions of density at different temperatures where a most extreme density was attained to at 900°C .

Wang et.al [3] studied the properties of glass ceramic derived from Blast furnace slag and nickel slag. The outcomes demonstrate that the with more amount of iron in the glass composition lowering the melting temperature, glass transition temperature (T_g), and glass crystallization temperature (T_c). The arrangement of the $\text{SiO}_2\text{-CaO-Al}_2\text{O}_3\text{-Fe}_2\text{O}_3$ system has a few specific crystallization qualities. Initially, the glass transition temperature (T_g) of the system is lower than the other system. Furthermore, Fe_2O_3 can be considered as great nucleating agent, and subsequently, the crystallization for this framework can be effortlessly figured it out. It is realized that in the $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-CaO-Fe}_2\text{O}_3$ (FeO) framework, Fe^{2+} as a net hole particle will pulverize the Si-O net structure and will diminish the viscosity of the glass, like Ca^{2+} and Mg^{2+} . Like Al^{3+} , Fe^{3+} will shape FeO_4 tetrahedrons and retouch the net structure creating the increment in viscosity of the glass. When the glasses have fewer alkali metals and alkaline-earth metals, Fe^{3+} will be situated in the gaps of the glass net structure and form FeO_6 octahedrons. Then again, when the alkali and alkaline earth metals are adequate, Fe^{3+} will oblige SiO_4 tetrahedrons and add to a more prominent viscosity of the glass melt.

Rawlings et.al [4] studied the production of glass ceramic from silicate wastes. Glass ceramic without extra TiO_2 shows the shallow exothermic peak which show that the surface crystallization

is predominant. With additional TiO_2 , the exothermic peaks were vastly improved characterized proposing that mass crystallization takes place. This prompted grain refinement of the crystallites. The Knoop hardness (1040kg/mm^2), the fracture toughness ($5.2\text{MPa}\cdot\text{m}^{1/2}$), and flexural strength (340MPa) for the 5wt% TiO_2 containing glass-ceramic.

A blend of steelwork slag, limestone, sand, bauxite, and ilmenite was utilized to create glass-ceramics with TiO_2 as the nucleating agents. The principle crystalline phases were diopside ($\text{CaMgSi}_2\text{O}_6$) and augite $(\text{Ca, Na})(\text{Mg, Fe, Al})(\text{Al, Si})_2\text{O}_6$.

Liu et.al [5] studied the crystallization and mechanical properties of glass ceramic developed by the ceramic-sintering process. Blast furnace slag with 5% potash feldspar gives glass ceramic with better mechanical properties. The main crystalline phase identified as gehlenite ($2\text{CaOAl}_2\text{O}_3\text{SiO}_2$) in the glass ceramic. A greater micro hardness of 5.2 GPa and flexural strength greater than 85 MPa and additionally a water absorption below 0.14% were obtained.

Rezvani et.al[6] studied the result of Cr_2O_3 , Fe_2O_3 and TiO_2 nucleating agents on the properties of glass ceramics. It was demonstrated that the simultaneous expansion of Cr_2O_3 , Fe_2O_3 and TiO_2 was more powerful to bring bulk crystallization in the system. It is a reasonable sign that with TiO_2 and Fe_2O_3 there is rapid mass crystallization and nucleation in the system in comparison to Cr_2O_3 added system. The Avrami parameter is showing the two-dimensional mass crystallization system affirmed from SEM images.

Khater [7] studied the effect of Cr_2O_3 , LiF, CaF_2 and TiO_2 nucleating agents on the properties of glass ceramic made from silicate waste. Cr_2O_3 and TiO_2 are a vastly superior comparison to LiF and CaF_2 in advancing uniform nucleation and the development of amazingly fine-grained microstructure of aluminous pyroxene and magnetite. The expansion of 2% TiO_2 to the glass batch enhances the crystallization of glass ceramic and melting of the glass composition. The occurrence of the TiO_2 nucleating agent gives the bulk crystallization in the system with the development of homogenous microstructure.

For glass in which the proportion of oxygen particles/network forming cations is more prominent than 2, there must be non-bridging oxygen particles, a bringing down of the free energy will take after if compound differentiation strikes give spaces in which the silica system is continuous and which are divided from one another by the non-bridging oxygen. Such a microstructure will give

a bigger number of potential nuclei for phases whose basic components are identified with the short-range arrange inside the spaces. It is proposed here that Ti^{4+} particles can make such areas by their propensity to possess the non-bridging surface destinations connected with non-bridging oxygen particles. This propensity is reliable with the limited capacity of Ti^{4+} particles to shape the stable tetrahedral system. Additionally, the dismissal of the Ti^{4+} particles to the periphery is normal since the solubility of Ti^{4+} in the system silicate structure is low. These criteria of considerations may be pondered facilitating the dissolving methodology, diminishing the viscosity of the resultant melts and expanding the crystallization ability of the relating glasses researched.

Mukherjee et.al [8] studied the effect of TiO_2 nucleating agent on the thermal and physical properties of glass ceramic processed from silicate waste. The crystallization kinetics and mechanical properties of SAC glass-ceramics were contemplated utilizing peak crystallization temperature (T_p) three distinct glasses as got from DTA, the activation energy (E) and Avrami exponent (n) were additionally decided. With increases the amount of TiO_2 agent in the system, peak crystallization temperature (T_p) and activation energy (E) increases. The studies demonstrated that the three-dimensional crystalline structure and the micro hardness expanded with the increment of TiO_2 . The prepared glass ceramic with highest (12%) TiO_2 substance indicated great mechanical properties with a hardness of 6.63GPa and density of 2.93g/cm^3 . TiO_2 substance expanded the glass framework demonstrated better crystallization and homogeneous grain arrangement. Three-dimensional and homogeneous crystal developments were seen with the increment of the TiO_2 content in the prepared glass ceramics.

Salama et.al[9] studied the influence of nucleating agents on the silicate glass ceramics. It was discovered essentially that the expansion of 10 wt% TiO_2 to the base glasses enhanced the batch melting and the crystallization ability of the glass through its mass. The presence of TiO_2 brought about a decline in the temperatures of softening by around 100°C and observably altered its crystallization kinetics. The DTA results showed that presentation of TiO_2 in the glass brought about a lowering of the temperature of the onset of crystallization by around 50°C . The Ti^{4+} occupancy of Si^{4+} destinations in the glass structure presents a Ti-O bond that is weaker than the Si-O bond. These prompts enhance the batch melting and crystallization ability of the glass.

Wu et. al [10] studied the influence of the high amount of TiO_2 in the glass-ceramic composition and effect on mechanical properties. A new glass-ceramic was created from an extra TiO_2 -

containing Blast furnace slag. The high amount of TiO_2 (20 wt %) in this system shifting oxide and increases crystallization in the glass system, bringing about a superior-grained material which have good mechanical properties ($E = \sim 120$ GPa, bending strength = ~ 180 MPa, and Vickers hardness = 7 GPa) after crystallization at 1100°C for 2 hours. The room temperature (RT) and elevated temperature fracture durability were additionally examined. The main crystalline phases found of pyroxene group until the heat treatment at 1000°C , after which titanium-rich perovskite and armalcolite crystals turned into the prevailing stages. The resultant glass ceramic is high-quality, tastefully worthy (metallic dark or misty cocoa shaded), and suitable for structural and building application.

The ideal measure of TiO_2 is subject to the constituents of the system and increments with diminishing SiO_2 amount. The subsequent polycrystalline material has better hardness, Young's modulus, bending and compressive qualities and great fracture toughness. The deciding item can possibly be utilized as load-bearing structural parts, e.g. high- temperature resistant machine components, and wear resistant segments in the building and building industry.

Barbieri et.al [11] studied the developing silicate glass ceramics from silicate wastes. They created cheap calcium alumino-silicate glass ceramics beginning from waste crude material containing huge percentage of Fe_2O_3 . The outcomes got demonstrate that the combined vitrification/devitrification procedure represents a suitable approach for the reusing and exploitation of coal fly ash and, specifically, of municipal incinerator slag. A lot of waste materials (40%–50% of coal fly ash and up to 100% of incinerator slag) are misused by this strategy, and it could be valuable in solving the critical disposal issue identified with these residues.

Ovecoglu et.al [12] studied the effect of TiO_2 on glass ceramic derived from Turkish blast furnace slag. With the addition of 3-5% weight of TiO_2 in the glass composition gives the main phase gehlenite ($\text{Ca}_2\text{Al}_2\text{SiO}_7$) and merwinite ($\text{Ca}_3\text{MgSi}_2\text{O}_8$). Heat treatment of glass at 950°C gives the big shape crystals which show the surface crystallization and at 1100°C small and more numbers of crystals found which shows bulk crystallization at a higher temperature. With increases the amount of nucleating agent in the composition, crystalline size decreases. These phenomena show that with increases the amount of TiO_2 bulk crystallization occurred. Also with increases the amount of TiO_2 in the glass composition, mechanical properties enhanced.

Shelestak et.al [13] studied the glass ceramic conversion of silicate waste from oil shales. After extracting oil from oil shales, the inorganic materials remains in shales are SiO₂, Al₂O₃, CaO, and MgO. This remaining silicate waste easily melted and converted into the glassy material. These shale glasses have great dielectric properties. The main composition is similar to the Blast furnace slag. The density found was 2.79 gm/cm³.

Folgueras et.al [14] studied the glass ceramic properties derived from Blast furnace slag and fly ash. SiO₂ and Al₂O₃ percentage found more in these silicate wastes. The high amount of CaO and MgO gives the strong base for glass. The more amounts of SiO₂ and Al₂O₃ gives the high melting temperature in the system. The Higher density found was 2.5gm/cm³ at 900°C. Crystallization started at 850°C.

Fredericci et.al [15] studied the thermal and mechanical properties of Blast furnace slag glass. The glass transition temperature (T_g) was found 742°C. The peak crystallization temperature (T_p) was found 1000°C. Merwinite was found as the main crystalline phase. After crystallization flexural strength decreases comparison to Parent glass. The Vickers hardness was found around 5.5 GPa.

Hauwaisa et.al [16] studied the utilization of silicate wastes for making glass ceramics. 2-20 wt% of TiO₂ gives fine microstructure in the glass crystallization. Using above 20 wt% TiO₂ crystallization decreases.

CHAPTER: 3

EXPERIMENTAL

PROCEDURE

Materials and Experimental Procedure

3.1 Materials:

(1) Blast furnace slag

(2) TiO_2

3.2 Chemical analysis:

Taken 0.4391 gm of Blast furnace slag in a platinum crucible and 10 gm of Na_2CO_3 and included few bit NaOH. Blended it legitimately and fuse the mass at 1000°C for 3 hrs. Chill it off move the mass in 70 ml HCL taken in a 250 ml beaker. Kept the container at the hot plate for overnight till complete drying. Then include 50 ml HCL and warm it and after this filtrate the mass through WHATMAN 540 filter paper, gather the filtrate 1 in a 250ml volumetric cup. Take the residue in a pre-weighted crucible fire at 1000°C for 1 hrs. The residue is accounted for as silica.

Determination of Mixed oxide (Fe_2O_3 and Al_2O_3):

Make the volume of a filtrate 1 up to the imprint taken 50 cc of filtrate 1 in a 250 ml container included couple of drops of Methyl red indicator (shading red in acidic medium), included ACC buffer till medium is alkaline (yellowish green shading) warm it and filtrate through WHATMAN 541 filter paper. Gather filtrate 2 in a 250cc volumetric flask. Fire the residue at 1150°C for 1 hrs. Report the residue as blended oxide.

Determination of Fe_2O_3 :

Taken 10ml of filtrate 1 in 250 ml funnel-shaped flask included 10cc of ammonium thiocyanate solution. Shading get to be dark red. Filtrate it against standard mercurious Nitrate solution with vigorous till shading less end point. Ascertain the measure of iron oxide from $\text{Ag}_2(\text{NO}_3)$ consumed report the distinction from the blended oxide as Al_2O_3 .

Determination of CaO and MgO:

Make up the volume of filtrate 2 and take 10 cc of filtrate 2 in 250ml cone shaped flask include 10cc AAC buffer and a squeeze of Eriochrome black T(EBT) indicator. Shading get to be wine red. Titrate it 17 standard EDTA arrangements (0.01M) to sky blue end point. Figure the measure of CaO and MgO from EDTA consumed.

Determination of CaO:

Taken 10ml of filtrate in cone shaped flask included NaOH arrangement (10%) and include a squeeze of P&R pointer. shading get to be light violet. titrate it with standard EDTA. Report CaO from the volume of EDTA consumed.

The final composition of Blast furnace slag determined:

Table 3.1 Blast furnace slag composition:

SiO ₂ (wt %)	Al ₂ O ₃ (wt %)	CaO (wt %)	MgO (wt %)	Fe ₂ O ₃ (wt %)
37.053	20.851	25.543	9.18	6.81

3.3 Batch preparation:

In the beginning of project chemical analysis and composition computation has been done. Blast furnace slag was received from Rourkela Steel Plant (SAIL-India). After that it was milled in Ball-mill with steel ball as grinding media inside it, for around 24 hours and changes into the fine powder form. Batch constituents finalize as:

Table-3.2 Batch composition:

	Blast Furnace Slag	TiO ₂
Batch-1(Wt %)	100	Zero
Batch-2(Wt %)	95	5
Batch-3(Wt %)	90	10

After finalized the composition amount, mixed all three batches properly. Batch constituents were finalized as:

Table-3.3 composition of glass ceramics:

composition	SiO ₂	Al ₂ O ₃	CaO	MgO	Fe ₂ O ₃	TiO ₂
Batch-1(wt %)	37.053	20.851	25.543	9.18	6.81	-
Batch-2(wt %)	35.2	19.8	24.26	8.72	6.47	5
Batch-3(wt %)	33.34	18.77	22.98	8.26	6.13	10

3.4 Sample Preparation:

This process comprises of following steps:

1. Batch mixing
2. Batch melting
3. Glass cutting
4. Ceramization
5. Specimen preparation for characterization

3.5 X-ray diffraction analysis:-

The crystalline phases were distinguished utilizing X-ray diffraction using Philips Diffractometer (model: PW-1830, Philips, Netherlands) utilizing Cu-K α radiation. The scanning range was selected for 2 θ from 20° to 70° on sample powder crystallized at different crystallization temperatures. The regular scan comprised of a step size of 0.04° with a 2-second hold every step. The measurement was done with scanning range from 20° to 70° on a powder layer of samples.

3.6 Differential scanning calorimetry (DSC):

The crystalline phases with variation in temperature were investigated by DSC (NETZSCH STA449C Thermal Analyzer). About 30 mg of powder specimen was kept in an alumina crucible and placed in the environment of argon. A-alumina was kept in another alumina (fused) crucible

as reference material. The temperature range for all specimen was fixed of 30–1000°C. The heating rate was taken at 5°C/min. DSC was employed to find out the crystallization peak temperature (T_c) and glass transition temperature (T_g).

3.7 Microstructure analysis by FESEM:

The FESEM is by far the most used for investigating the microstructure of a crystalline solid which may consist of one or more phases. Corresponding grain-shape, grain-size, packing of grains, grain boundaries, pore, micro-cracks and their size are revealed by this important material characterization technique. The glass ceramic specimen heat treated at different temperatures were cut down into required shape. The sample surface is cleaned in the ultra-sonicating bath before testing. After the cleaning the samples, gold coating was applied on samples and fixed on sample holders in FESEM. Gold coating is used as most of the ceramic samples are insulating. After these processes, FESEM investigation performed on samples.

3.8 Bulk density analysis:

Bulk Density (B.D.) is characterized by the application of Archimedes's principle to discover how much material is confined in a specific volume. Thus, it is the proportion of the mass of a material to its mass volume, i.e. the volume of the given material in addition to all the pores inside it. In structural application, the bulk density is given importance as it estimates how much material is required and the estimated price correspondingly.

Evacuation method is used for determining the bulk density of the samples. First, the weight of the specimen is measured and noted down. This weight is known as dry weight (D). Now the sample is put in a desiccator and afterward is evacuated to allow the trapped air to come out of the specimen. After this, specimens are immersed fully in kerosene suspending from a hook in a digital balance and weighed. This weight is known as suspended weight (S). At that point, the specimens are dried out utilizing kerosene-soaked cloth. Now splashed weight (W) is measured.

$$\{B.D. = [D / (W-S)]\}$$

Where D is Dry weight, W is Soaked Weight and S is Suspended Weight

3.9 Flexural strength of glass ceramics:

Flexural strength is also called the 3-point bending or Modulus of Rupture. It is a mechanical property for determine the strength of the material. It is described as a material capacity to oppose deformation under load.

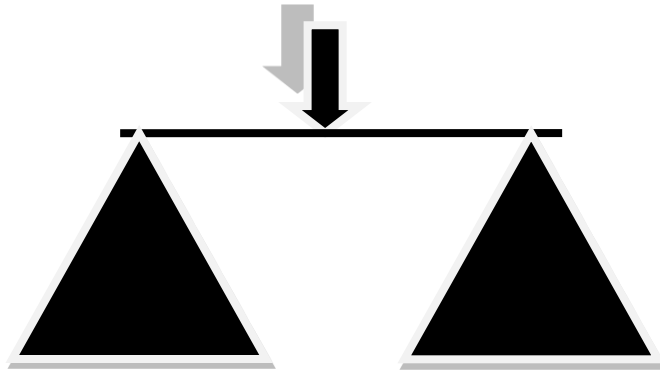


Figure-3.1 Flexural strength mechanism

Samples measured and cut down into a long rod shape. Take the samples and put down the sample on the edges of the sample holder and after that load applied at the center of specimen gradually. The maximum load at which specimens break down, noted and the flexural strength calculated by the equation.

$$\{M.O.R=3WL/2bt^2\}$$

Where,

W is the maximum load (N),

L is the Distance between two bearing edges (cm),

b is the Width of the sample (cm),

t is the Thickness of the sample (cm).

3.10 Vickers Hardness:

Hardness is the property of a material that permits resistance to plastic deformation, by indentation. Hardness is like one kind of resistance offered by material to rubbing, bending and cutting. In Vickers hardness testing, the specimen is indented with a diamond indenter, as a right pyramid with a square base and a point of 136 degrees between inverse appearances. A 0.5kgf load is applied to the specimen. The loading period on specimen was given 10 seconds. Mark the area of two diagonals of the load indentation on surface measured by the microscope which connected with the computer. Now the indentation area is calculated. The value of Vickers hardness is obtained by the equation.

$$HV = 1.854F / \text{area of indentation } (d^2)$$

Where, F = load (kgf)

d = avg. of indentation (mm)



Figure 3.2 Vickers hardness testing machine

3.11 Compressive strength (CCS):

The compressive strength is the most extreme compressive stress of a material is able of withstanding without crack. Fragile materials break during testing and have a distinct compressive strength value. The compressive strength of ductile materials is dictated by their level of bending during testing. The compressive quality testing is performed in Universal Testing Machine (UTM). The first glass ceramic sample cut down into cube form and measured the dimensions and note down the readings. The sample put down between the compressive plates of UTM at the middle point. This arrangement done like when the load is given, the load is connected to the sample with the upper plate. The load given gradually and measured with time by using computer attach with the UTM. The load is gradually increased until sample breaks. The Maximum load at which sample fails is write down, and this is highest force (F_{max}). The surface area of the base is ascertained and after that compressive strength can be figured.



Figure 3.3 Universal Testing Machine (UTM)

$$\text{Compressive Strength} = F_{max} / L_1 \times L_2$$

Where, F_{max} = Max. Force at which sample fails

$L_1 \times L_2$ = area of the specimen

3.12 Dilatometry Test:

A dilatometer is an experimental instrument that measures volume changes brought on because of any physical or substance process. Dilatometry is additionally used to oversee the advancement of chemical reactions. Estimation of thermal extension is the basic use of a dilatometer. Connecting rod (push bar) dilatometer was utilized to discover the sintering and shrinkage conduct and the scope of temperatures.

Thermal expansion of sintered bar formed specimen was determined over by NETZSCH dilatometer model DIL 402 C. In the dilatometer; the sample is kept in a sample holder in the focal point of the furnace. The linear dimensional change i.e. expansion or shrinkage of the sample is transmitted through the push bar (squeezed against the specimen inside the furnace) to the measuring head. Tests size was a bar having width 6 mm and length 15 mm for dilatometer test. The warming rate was kept up at 10°C/min. The measurement was completed from room temperature to 900°C in argon environment.



Figure-3.4 Dilatometry machine

CHAPTER: 4

RESULTS

AND

DISCUSSION

4.1 Determination of glass-melting temperature of BF-slag:

Melting temperature is the temperature at which the material start conversion solid to liquid. In order to investigate the melting temperature all three batches named as 'Batch1', 'Batch2' and 'Batch3', some pellets are made with cylindrical die-punch and electrically operated automatic hydraulic pressing machine. Pellets of each composition were put into the furnace at different temperature and soaking time and the deformation if occurred at all were noticed.

At 1100°C sintering happens yet no liquid was seen to emerge from the specimen of all composition. At 1200°C, pellets of all composition get softened and it could be concluded that eutectic temperature had been reached. At 1300°C halfway melting happens, and eutectic creation is finished. At 1300°C, the soaking time was expanded and because of that some additionally softening stages framed and a few bubbles begin turning out from the Batch. At 1350°C the group doesn't soften totally as a result of high alumina in the system however bubble development proceeds. The air bubbles attempt to turn out however because of the high viscosity of melt they don't go away completely. At 1400°C, batch softens totally and appearance of the bulk sample was seen to be transparent like glassy phase. At this stage, bubbles were not seen as that might have escaped from the melt most likely. This helps in presuming that melting temperature of the system was 1400°C. Another observation was made that the colour of the Batch changed during melting procedure. This fact was due to the presence of Fe_2O_3 to some extent in BF-slag.

4.2 Glass-ceramization

Glass samples were heat treated at the temperature 800°C, 900°C, 1000°C and 1100°C with a soaking time of 4 hours to prepare the glass ceramic. At the end of the heat treatment process, the changes in appearance were examined after taking out from furnace.

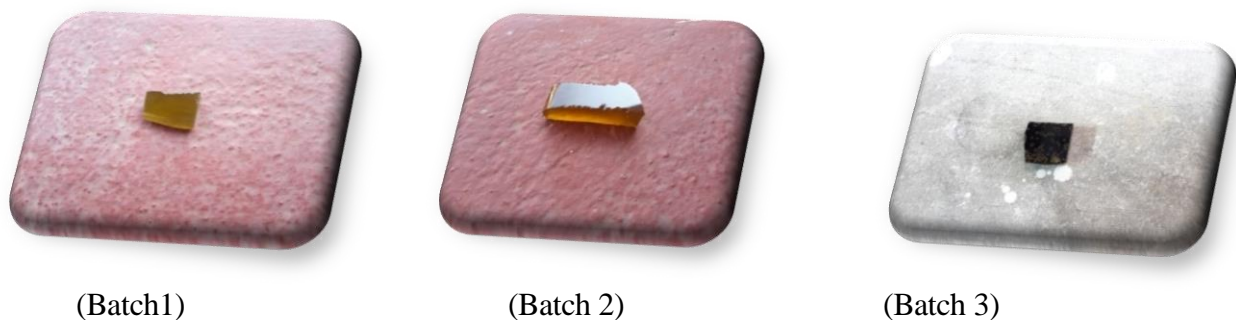


Figure-4.1 Glass crystallization at 800°C

After heat treatment at 800°C for 4 hours, it has been seen that there is no such difference in the transparency of the glass samples. Though the appearance is not purely transparent rather translucent. The grayish color is attributed to the presence of Fe_2O_3 and well explained by ‘ligand field theory’ in some solid state chemistry textbooks. Here with Fe_2O_3 added TiO_2 has some effect in making the colour of glasses that is why three batches have different colour. So it is concluded that after heat treatment at 800°C there is no nucleation in all specimens. Batch1, Batch 2 and Batch3 heat treated at 800 °C/4hr should not be identified as glass-ceramics but glass only.

The next step to heat-treatment at 800 °C was a heat treatment of glass specimens of Batch1, Batch2 and Batch3 at 900°C for 4 hours. Again the visual appearance of three compositions was observed to make a decision whether nucleation has started at all or not. In Fig.4.2, the photographic images have been given for the above mentioned heat-treated specimens.



Figure-4.2 Glass crystallization at 900°C

The transparency of the glass samples had gone away totally, and those could be called as the opaque body. The viscosity of the glass network has been decreased which assist in the diffusion of different cations (viz. Ca^{2+} , Mg^{2+} and Ti^{4+} etc.) inside the glassy network. As the diffusion barrier is surmounted, ions leave the glassy matrix and joins the as of nucleated primary crystal to grow as crystallites. Eventually, presence of multigrain in glass-ceramic prevents propagation of light as there is mismatch in the orientation of grain to grain. Accordingly, the glass-ceramic body is getting opaque appearance. In addition to that the heat-treated specimens were noticed to get shrunk significantly.

The crystallization process should be assumed to be completed while the glass specimens of all three compositions are subjected to heat-treatment at 1000°C for 4 hours. Fig.4.3 depicts the visual status of glass-ceramized specimens.

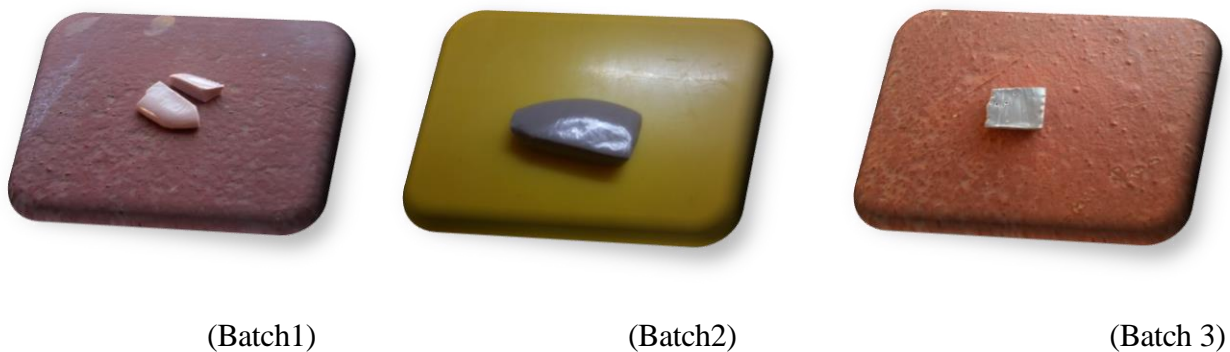


Figure-4.3 Glass crystallization at 1000°C

It has been noticed that the glass has changed into an opaque body. In this case, significant shrinkage happened to all heat-treated specimens as happened to 1000 °C for 4 hr. heat-treated samples.

When the glass heat treated at 1100°C for 4 hours, as represented at Fig.4.4, it has been observed that there is no more change in samples. Hence, maximum crystallization has been occurring before 1100°C, which has been supported by XRD test results.



Figure-4.4 Glass crystallization at 1100°C

4.3 X-ray diffraction (XRD) analysis:

XRD analysis was proved to be very important material characterization technique as that is capable of giving information regarding phases present in the bulk as well as quantification of phases. At present, though exact quantification had not been carried out, the relative amount of glass to crystal phase could be estimated by comparative analysis as per the Fig.4.5.

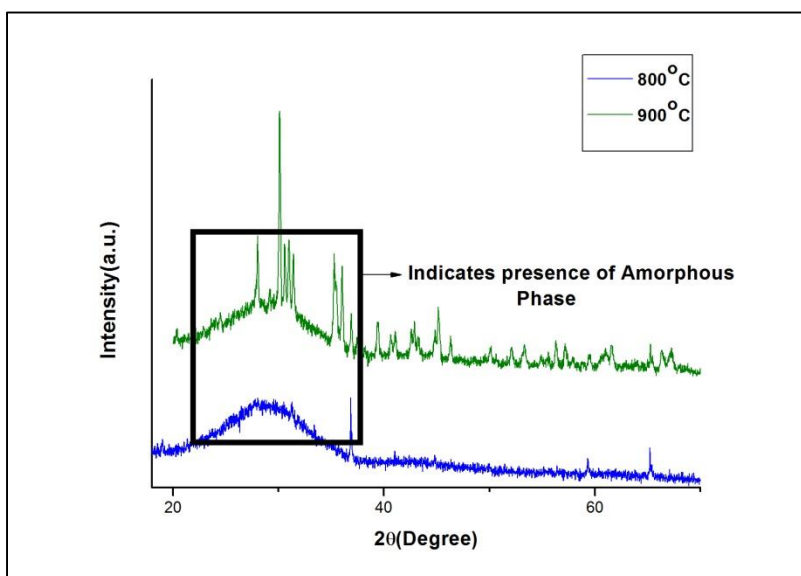


Figure 4.5 XRD Pattern of Batch1 heat-treated at 800°C and 900°C

Fig. 4.5 exhibits the coexistence of glassy phase and crystalline phase for Batch1. As the heat-treatment temperature was increased from 800 to 900 °C, the changes appeared which could be identified from the above figure. The details of crystalline phases are discussed in the subsequent figure. Fig. 4.6 to 4.8 demonstrates the XRD diffraction patterns of Batch1, Batch2, and Batch3 consequently. Batch1, Batch2, and Batch3 of glass-ceramics with different quantity of TiO_2 were fabricated with varying heat-treatment temperature. Diopside ($\text{CaMgSi}_2\text{O}_6$) and Gehlenite ($\text{Ca}_2\text{Al}_2\text{SiO}_7$) was found as major phases with the help of XRD. Through the crystallization route, alkali oxides broke the matrix of glassy network and minimized the fraction of link oxygen. This could affect the change of octahedral magnesium groups $[\text{MgO}_6]^{10-}$ in tetrahedral groups $[\text{MgO}_4]^{6-}$. The majoring octahedrons had a tendency to join with $[\text{SiO}_3]^{2-}$ and $[\text{CaO}_6]^{10-}$. This phenomenon leads to the development of diopside ($\text{CaMgSi}_2\text{O}_6$) phase.

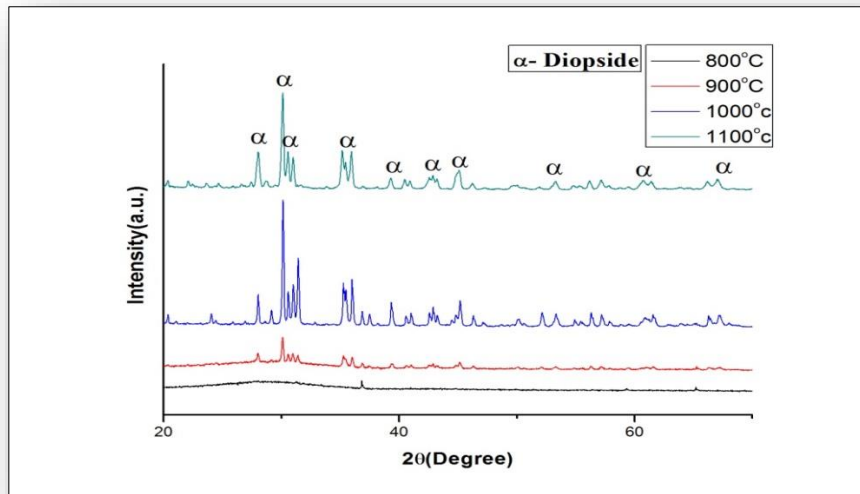


Figure 4.6 Batch-1 XRD Pattern at different crystallization temperature 800°C, 900°C, 1000°C and 1100°C

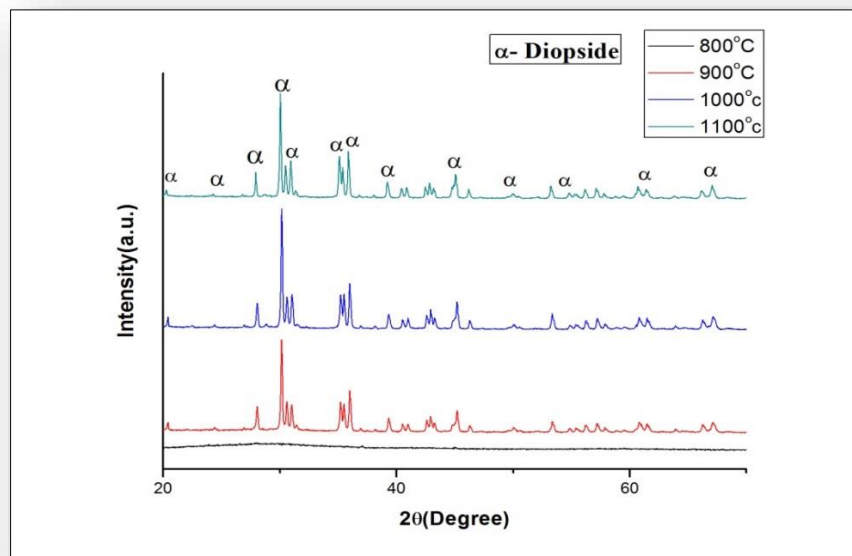


Figure 4.7 Batch-2 XRD Pattern at different crystallization temperature 800°C, 900°C, 1000°C and 1100°C

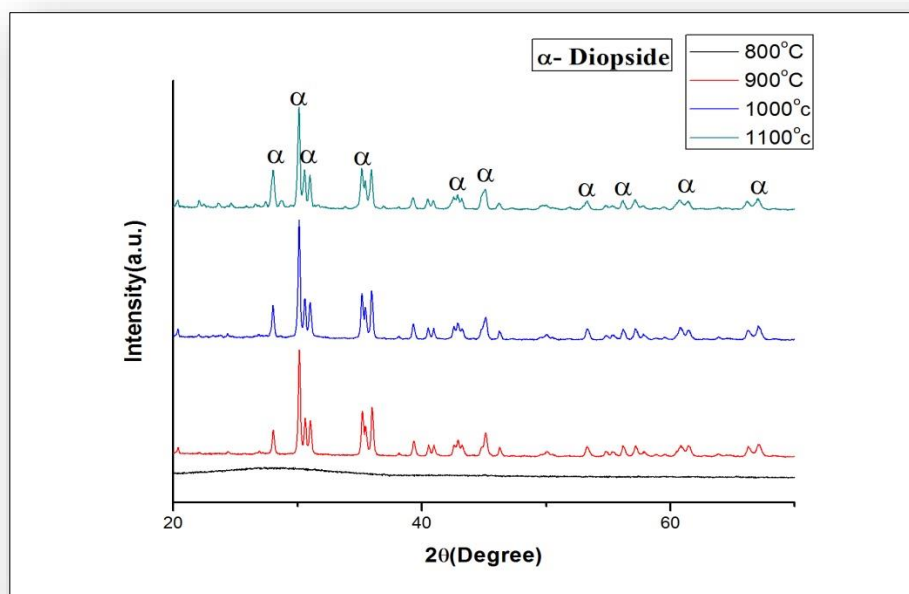


Figure 4.8 Batch-3 XRD Pattern at different crystallization temperature 800°C, 900°C, 1000°C and 1100°C

At 800°C XRD shows the amorphous nature of all three batches as crystals are not emerged in microstructure to give peaks. XRD peaks are expected if there is the presence of periodic arrangement of atoms in the crystalline state. With increasing temperature, the extent of crystallization increases and some peaks with relatively high intensities suggests that crystallite some amorphous phase still present in the system at 900°C. At 1000°C peaks are much finer as compared to 800°C and 900°C, which shows more crystallization compared to at 800°C and 900°C. At 1100°C, the peaks are finer but peak intensity is lower than 1000°C which shows melting of phase, which has been supported by DSC and FESEM test results.

A melting phase is starting to show up at 1000°C reveals the fully vanishing of anorthite crystalline phase. This result can be related with DSC result which shows a peak around 920°C. The endothermic peak seen at 930°C may be because of the commencement of dissolution of both Diopside and gehlenite phases. The thermal expansion coefficient of the glass ceramic shows an average rate of $7.444 \times 10^{-6}/^{\circ}\text{C}$ (30–400°C) which lies in the comparable range of phase pure Diopside. With increasing amount of addition of TiO_2 (5 to 10 weight %) peaks intensity increases, which exhibits that glass-ceramics obtained from batch3 has larger crystallite size.

4.4 Microstructure analysis:

To study the phase evolution with increasing heat-treatment temperature FESEM images has been analyzed. The parent glass is based on the material system as $\text{MgO-CaO-Al}_2\text{O}_3\text{-SiO}_2$ where the Fe_2O_3 and TiO_2 are also present.

4.4.1 Microstructure of glass-ceramics obtained from Batch1

Fig. 4.9 represents the glass-ceramics obtained by heat-treatment at 900/4hr, 1000/4hr, and 1100 °C/4hr. Fig.4.9 shows FESEM pictures of Batch-1 samples. As seen in Figures, it is evident that glass-ceramics of Batch1 is mostly amorphous phase at 900 °C, a few crystallites appeared in glass matrix which are known as diopside ($\text{CaMgSi}_2\text{O}_6$) belong to pyroxene group of minerals.

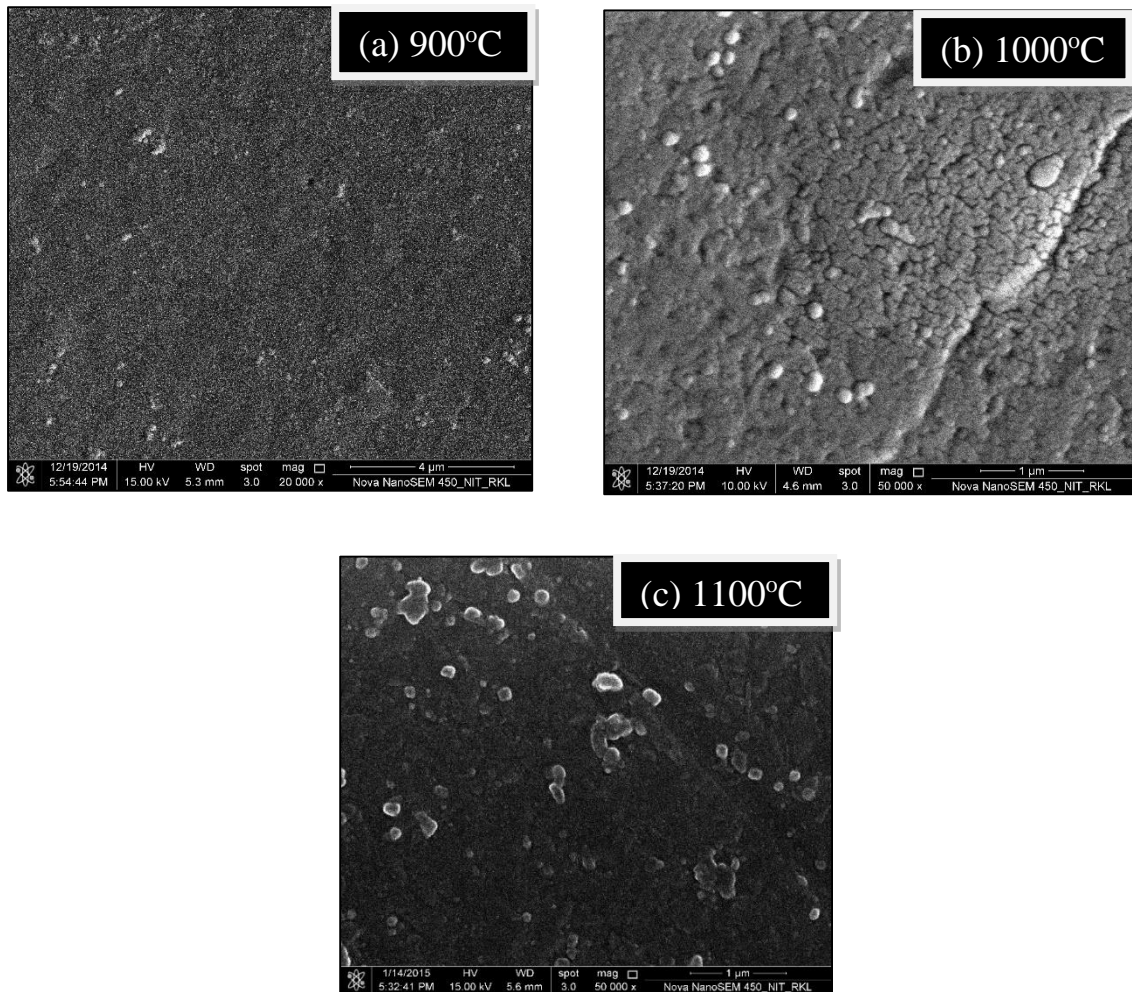


Figure-4.9 FESEM images of Batch1 heat-treated at 900°C, 1000°C and 1100 °C/4hr.

Figure (b) demonstrates significant crystallization at 1000°C as spherical grains appeared with raising the temperature. Figure (c) establishes the fact that there is melting of fully developed grains at 1100°C. So it could be concluded that crystallization phenomena are limited to 1000°C heat treatment.

Energy dispersive Spectroscopy (EDS) of Batch1 has been represented by the sub session because elemental analysis as well as elemental tracking is obtainable while examining the microstructure of materials. Though this analysis has shortcomings to reveal the bulk nature of sample still, one could be able to get a microanalysis. Several aspects are coverable in the micro-structural analysis to describe the glass-ceramic structure which is of current interest.

First of all a qualitative analysis could be represented with the following information. EDS of the glass-ceramic specimen Batch1 has been represented in Fig.--- that reveals the intensity peaks of the elements Al, Si, Mg, Ca, Fe, Ti and O. The converted weight percentages to oxide from respective element are comparable to experimental data obtained in chemical analysis. It is noticeable that a few percentage of TiO_2 is present in the level of impurities. That might have come along with the mineral ore Fe_2O_3 .

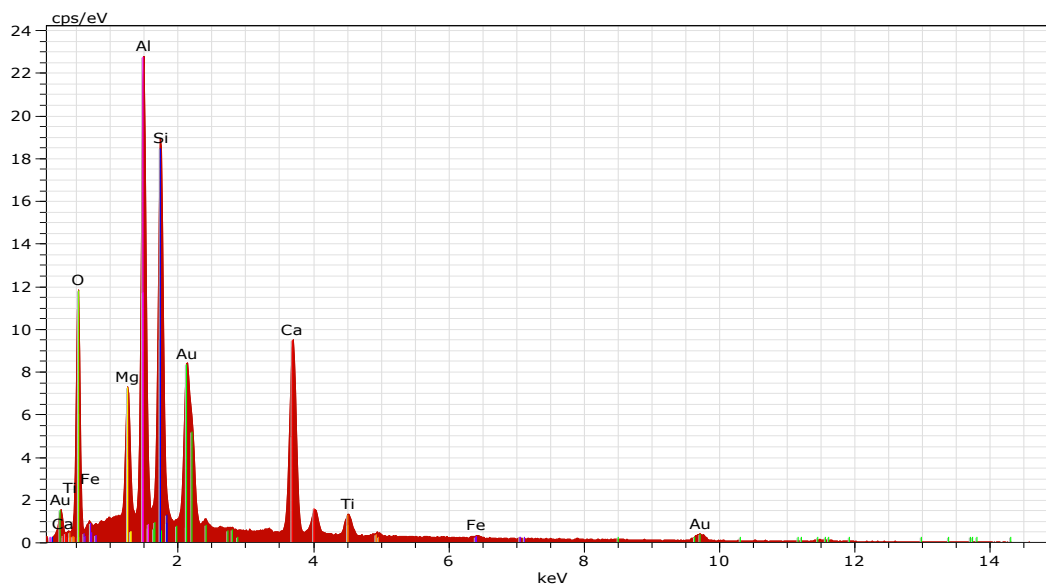


Fig.4.10 EDS spectrum of glass-ceramic from Batch1 heat-treated at 1000 °C/4h

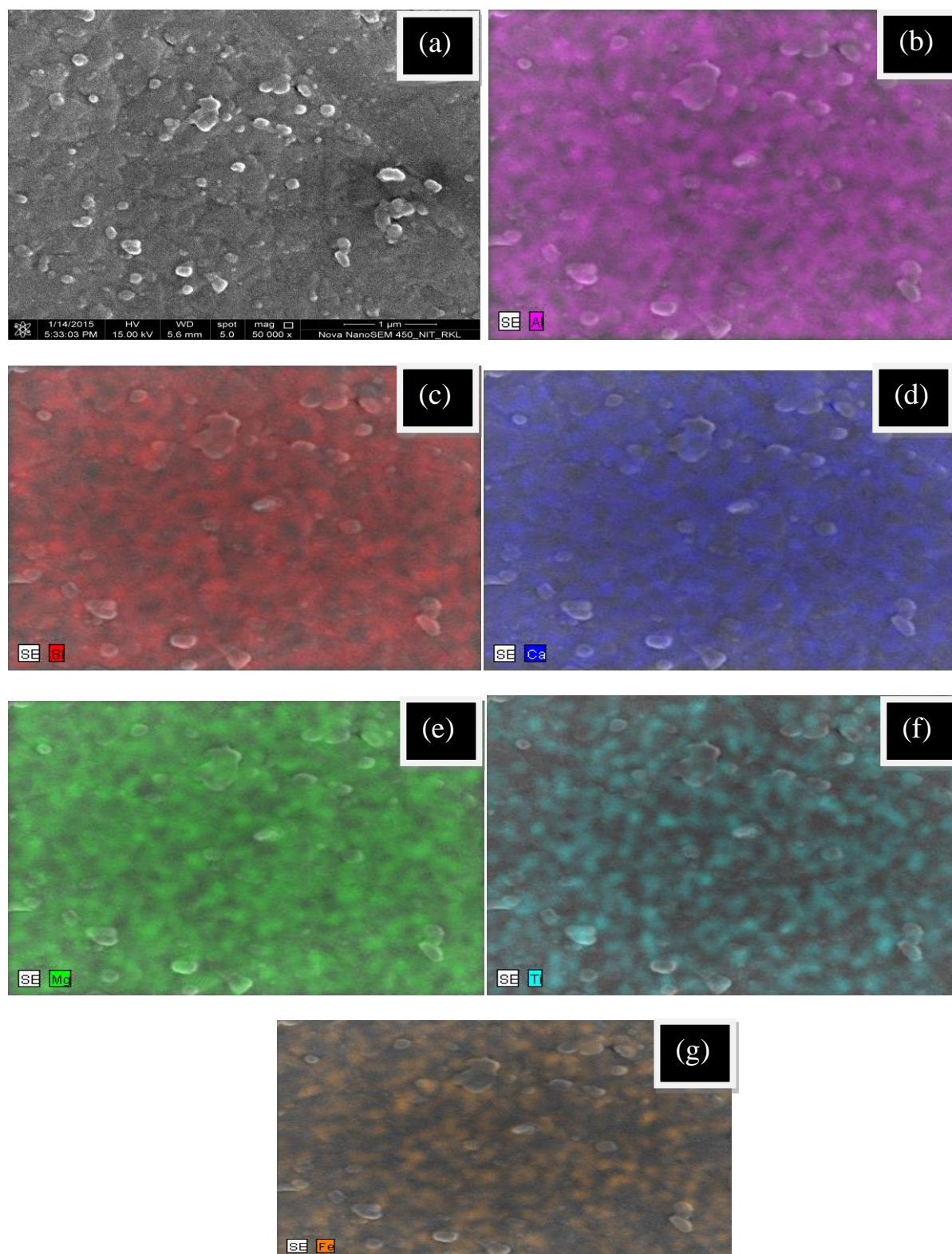


Fig. 4.11 Elemental mapping of glass-ceramic obtained after heat-treatment of Batch1 at 1000°C/4hr. (a) Secondary Electron image (b) Al (c) Si (d) Ca (e) Mg (f) Ti and (g) Fe

Elemental mapping of glass-ceramic of Batch1 at 1000°C/4hr has been represented to study the elemental distribution within glass-ceramic. It was believed that heat-treatment at 1000°C is enough to complete the crystallization. So it would be rational to analyze images from the glass-ceramic with maximized crystallization.

From the figure above, one can clearly understand that the developed crystallites are of Fe-riches Magnesium Titanium Silicates, where SiO₂ occupying the residual glassy matrix as well as that has depleted in the centre of the crystalline areas.

4.4.2 Microstructure of glass-ceramics obtained from Batch2

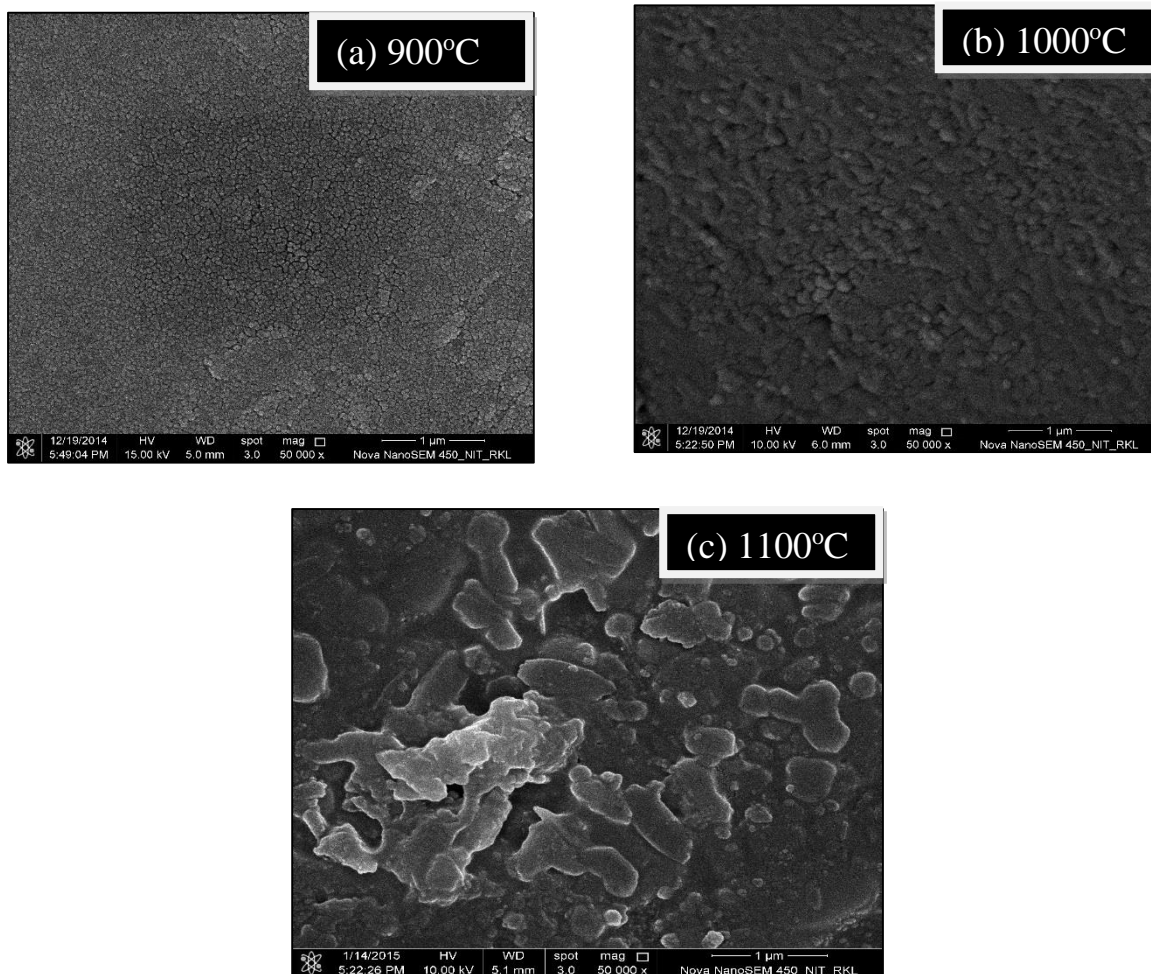


Figure-4.12 FESEM images of Batch2 heat-treatment temp. 900, 1000 and 1100 °C/4hr

From Fig. 4.12, it could be observed that the nucleation, as well as crystallization, has been seen increased in significant extent with addition of 5.0 weight% of TiO_2 , as compared to Batch1 which has been supported by characterization with FESEM. From the Fig. 4.12 (a), it could further notice that at 900°C , glass matrix is almost replaced by tiny crystallites. That clearly indicates that the added TiO_2 has been able to create heterogeneous sites for volume nucleation.

XRD and flexural strength analysis results (discussed in the subsection 4.2 and 4.8 respectively) also support this result. Batch2 images show that more crystallization takes place over samples due to more TiO_2 including. There is more number of crystals has been formed because of the additional nucleating agent (5% TiO_2). Because Ti^{4+} ions partially substitute of Si^{4+} sites in the glass network to form Ti-O bond that is weaker than the Si-O bond. This event enhances the batch melting and consequently crystallization of the glass. Figure (c) reveals the melting of crystals at 1100°C heat treatment, which is responsible for the decrease in crystallization.

Figure 4.13 represented EDS spectrum of Batch2 glass-ceramic heat-treated at $1000^\circ\text{C}/4\text{hr}$ that depicts the elemental presence in the glass-ceramic sample. The counts appeared from the representatives of Si, Mg, Ca, Al, Fe, and others as an element are well agreement with the chemical analysis and XRD analysis.

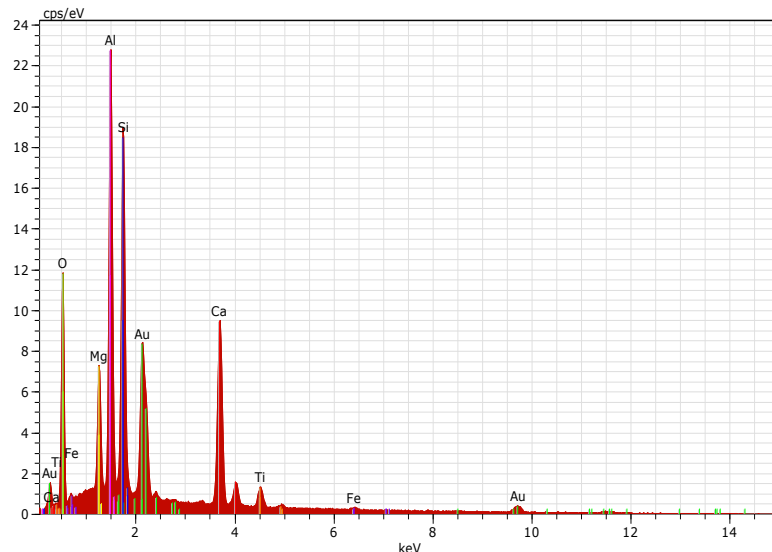


Fig.4.13 EDS spectrum of Batch2 glass-ceramic heat-treated at $1000^\circ\text{C}/4\text{hr}$

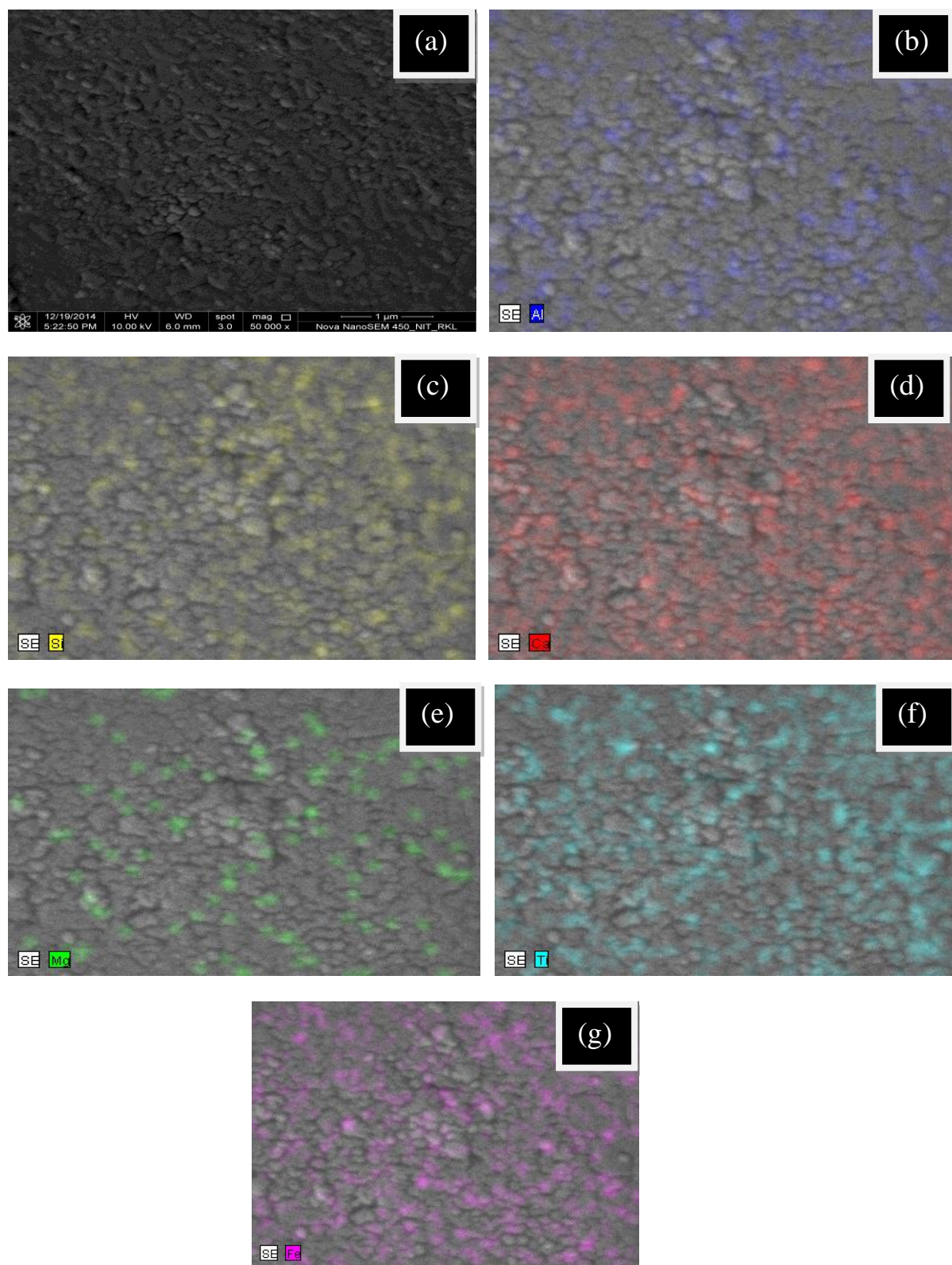


Fig. 4.14 Elemental mapping of glass-ceramic obtained after heat-treatment of Batch2 at 1000 °C/4hr. (a) Secondary Electron image (b) Al (c) Si (d) Ca (e) Mg (f) Ti and (g) Fe

In the Figure 4.14, elemental mapping of glass-ceramic of Batch2 at 1000°C/4hr has been given. It was studied that primary phases of TiO_2 are homogeneously distributed within bulk of glass-ceramic. It was believed that heat-treatment at 900°C is enough to complete the crystallization. So it would be rational to analyze images from the glass-ceramic with maximized crystallization.

4.4.3 Microstructure of glass-ceramics obtained from Batch3

From the figure above, one can clearly understand that there is nucleation at 900 °C throughout the matrix. At 1000 °C, significant growth has been occurred to a few crystals and finally dissolution has been seen to occur at 1000 °C to the glass-ceramic of Batch3.

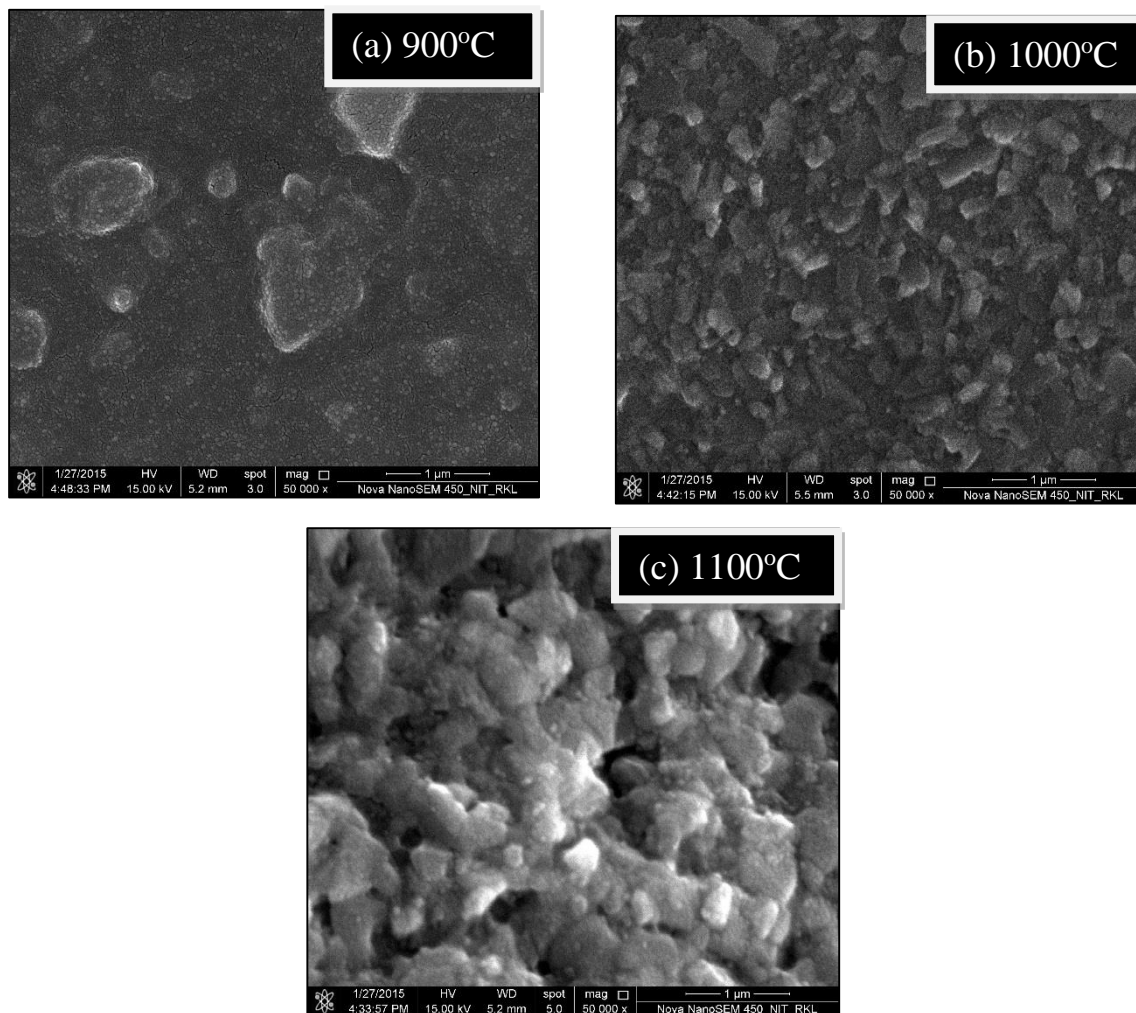


Figure-4.15 FESEM images of Batch3 heat-treated at 900, 1000 and 1100 °C

As seen from the above Figure, clearly the amorphous phase is present in fewer amounts to notice in glass-ceramics from Batch-3. With increasing temperature, the corners and edges are seen to be rounded that is evident from Fig 4.15 (c). That reveals the dissolution of crystal phase had occurred as a result of high thermal activation. Figure (b) show the more number of crystals comparison to the Figure (a), which means there is more crystallization at 1000°C in comparison to crystallization at 900°C. Figure (c) shows the crystallization at 1100°C, reveals the melting of crystals.

The FESEM results demonstrate that the less crystallization in Batch1; higher crystallization is predominant in Batch2 and Batch3. Thus, crystallization have an effect all over the whole volume in the Batch2 and Batch3. this result shows that with increasing TiO_2 , there is more crystallization. Ti^{4+} substitutes Si^{4+} sites partially in the process of making glass-ceramization, in reality there is the formation of primary crystals of MgTiSiO_5 and CaTiOSi_5 at near about 900 °C. Finally, there are diopside and gehlenite in the microstructure of Batch2 and Batch3 heat-treated at 900 and 1000 °C/4hr. But at Higher Temperature 1100°C we can see, there is some melting of phases which supported by XRD and DSC results analysis.

4.5 Differential scanning calorimetry (DSC) analysis:

Fig.4.16 reveals the DSC curves of the all three Batch glass samples. The small endothermic peak (780–790°C) shows the atomic rescheduling in this temperature range. This temperature is known as Glass transition temperature (T_g). The exothermic peak (T_p) (790–900°C) shows the crystallization behavior of glass system. This temperature is known as the '*crystallization temperature*'. Batch1 test with no added substance has a little exothermic top, while Batch2 and Batch3 tests containing 5 wt% and 10 wt% TiO_2 independently have wide and clear exothermic tops, which show the great crystallization capacity. Thus, a glass-transition temperature was found in the range of 780-790°C, and a nucleation temperature was found in the range of 790-900°C. A sharp endothermic top shows up at 920-930°C proposing some crystals have started to melt, which has been supported by XRD and FESEM test results.

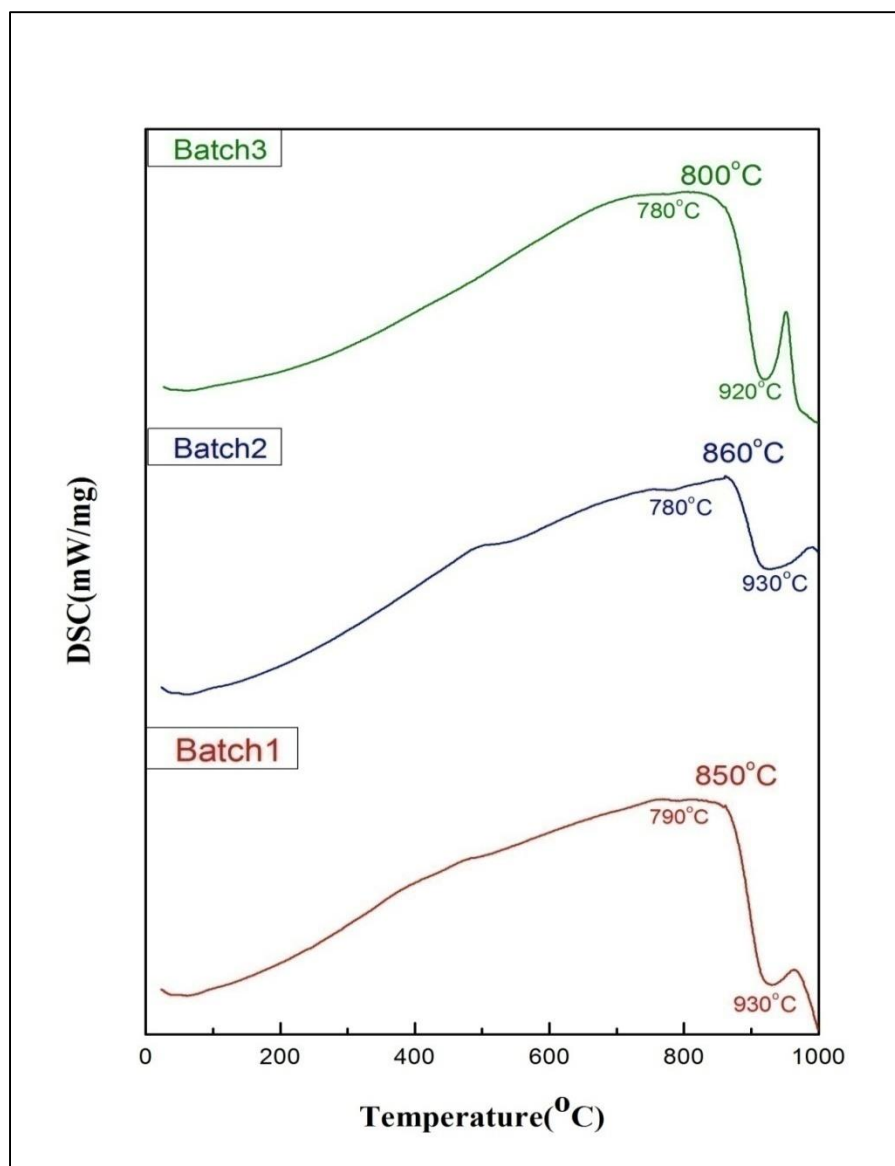


Figure-4.16 DSC graph of Batch1, Batch2, and Batch3

In Batch3, crystallization temperature (T_c) is less than Batch1 and Batch2 crystallization temperature (T_c), which shows that crystallization rate is very high in Batch3 because of less gap between Glass transition temperature (T_g) and crystallization temperature (T_c). TiO₂ gives the rapid crystallization in Batch3. In Batch1, a broad endothermic peak occurs at 930°C shows the melting of some phase, and reveals that the surface crystallization is predominant in Batch1 system. It can be seen in pictures that there is less crystallization in Batch1 because of the absence of nucleating agent and also there is surface crystallization is the main crystallization mechanism in Batch-1.

4.6 Studies on Bulk Density:

Bulk density was measured by Archimedes principle and the data found are tabulated below:

Table 4.1 Density values of glass ceramics

Varied heat-treatment temperature → Composition ↓	Bulk Density(gm/cc)				
	Parent Glass	800°C	900°C	1000°C	1100°C
Batch1	2.894	2.896	3.0	3.06	2.973
Batch2	2.90	2.907	3.0	3.02	2.992
Batch3	3.15	3.46	3.55	3.57	3.53

The data reveals that the density changed with temperature and amount of TiO₂. The density of parent glass did not change at 800°C, shows that no crystallization happens at 800°C. Also, we can see from XRD that no crystallization happens at 800°C. The density begins to be efficient at 900°C and reaches at a higher value at 1000°C.

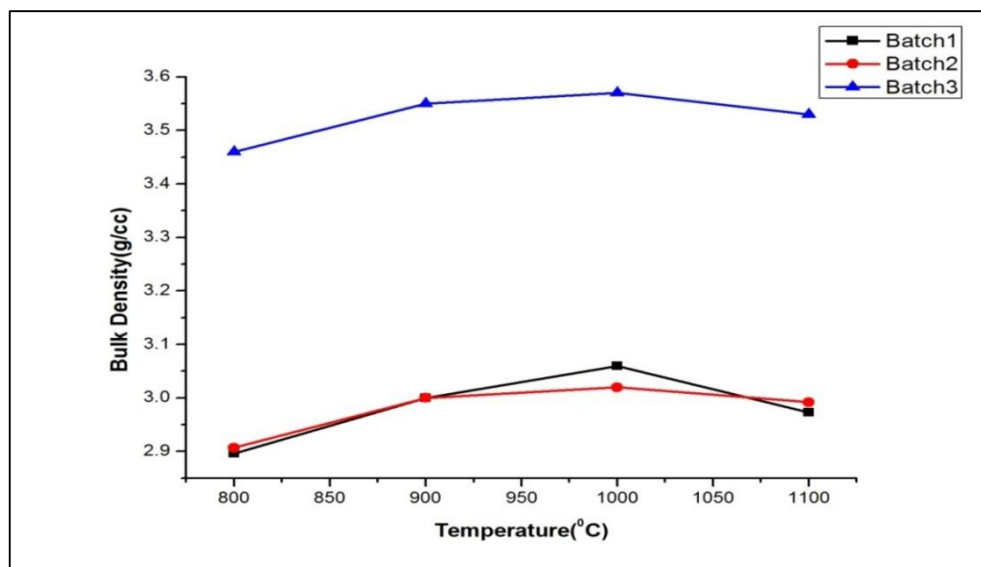


Figure-4.17 Bulk density vs. temperature

As shown in diagram density increases with increase in temperature as 1000 °C. This fact suggests that crystallization of glass-matrix is almost over to that temperature. Beyond 1000 °C, B.D. value decreases as there is the dissolution of crystals to glass. Obviously the disordered structure of glass should increase much more volume to bulk glass-ceramics. This phenomenon was well visualized with microscopic images of glass-ceramics of Batch1, Batch2 and Batch3 earlier in the subsection 4.4.

The density of Batch 3 shows comparatively much more density perhaps due to the nucleating effect caused by the extraneous addition of TiO₂ (5 to 10 weight%). The increment in density could be well explained by the fact that more and more glassy phase diminishes while increasing the heat-treatment temperature from 900 to 1000 °C.

4.7 Hardness of glass ceramics

Hardness of the all three Batch compositions was reported in table 4.2:

Table 4.2 Hardness of glass ceramics at different temperatures

	Hardness value (Hv)			
Composition	800°C	900°C	1000°C	1100°C
Batch1	680	858	730	696
Batch2	700	865	805	744
Batch3	735	892	864	791

It can be seen in Batch-3, which is having a higher amount of TiO₂, has a higher strength. Therefore, it has been cleared that significant crystallization has occurred while using TiO₂ as nucleating agent. The extent of crystallization strengthens the glass-ceramic structure as glass/crystal interface is minimized with decrease amount of glass. The amounts of glass in glass-ceramics samples are bound to decrease as crystals grow at the expense of glass compositions in the matrix. Alumina silica phase gives high hardness value. Consequently, there is an increment in surface hardness as there is more crystals site accessible at the surface. Then again, Batch 2, having a lower TiO₂ substance has a low hardness value and Batch1 having less hardness comparison to batch 2 and batch3.

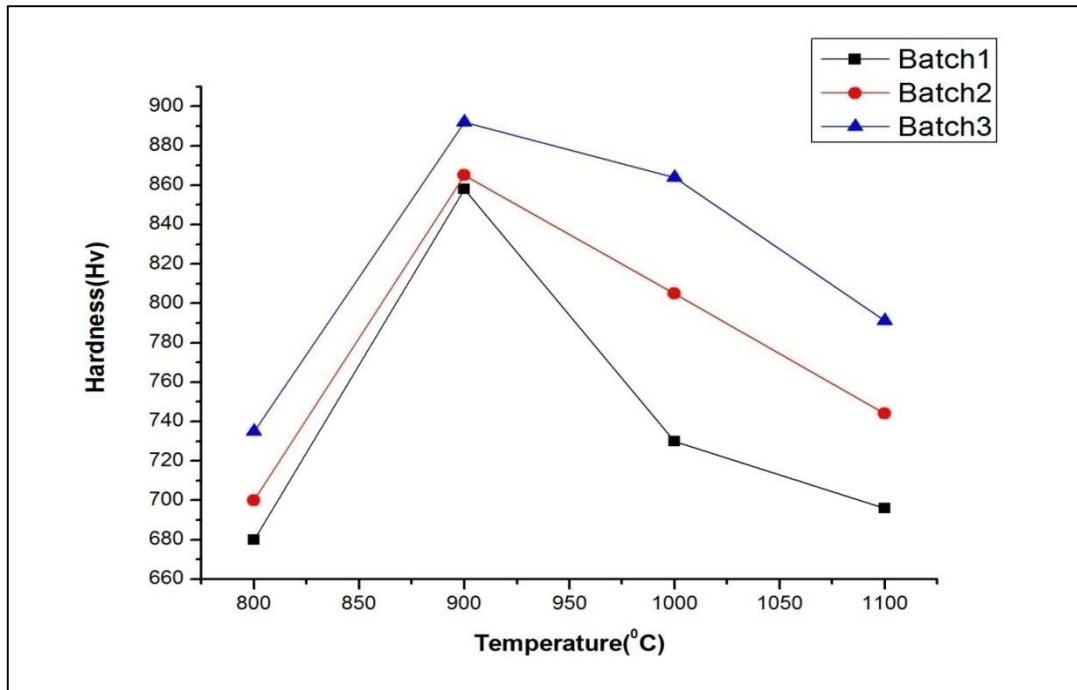


Fig. 4.18 Hardness vs. temperature

But treating the glass above 900°C the hardness value decreases indicating that the surface crystals are melting due to high-temperature treatment. There is fewer crystals site accessible at the surface after 900°C, which leads to the decrease in hardness value.

With increasing amount of TiO_2 , Hardness value also increases due to the higher crystallization with comparison to without TiO_2 system. Because Ti^{4+} Takes the place of Si^{4+} destinations in the glass network presents a Ti-O bond that is weaker than the Si-O bond. These prompts enhance the batch melting and crystallization ability of the glass. Also FESEM support that higher crystallization present in TiO_2 system, whereas less crystallization is present in without TiO_2 system.

4.8 Flexural strength of glass ceramic

The flexural strength has been calculated for each batch as below:

Table 4.3 Flexural strength of glass ceramics heat-treated each at 1000 °C/4hr

Sample	Flexural strength(MPa)
Batch1	20.57
Batch2	31.28
Batch3	42.65

For batch 1, the flexural strength was found to be 20.57 MPa with a maximum extension of 0.109 mm. For batch 2, the flexural strength was found to be 31.28 MPa with a maximum extension of 0.091 mm. For batch 3, the flexural strength was found to be 42.65 MPa with a maximum extension of 0.089 mm. A higher percentage of nucleating agent TiO_2 in Batch 3 prompts more crystallization and hence gives higher strength. Likewise, the fragility because of the glassy stage is lower. As there are more sites for nucleation accessible consequently, crystallization is more. Crystal phases are inserted in a glassy framework which offers high resistance towards the crack propagation. Consequently, the glasses ceramic which have additionally nucleating operators have more crystallization shows more flexural strength value.

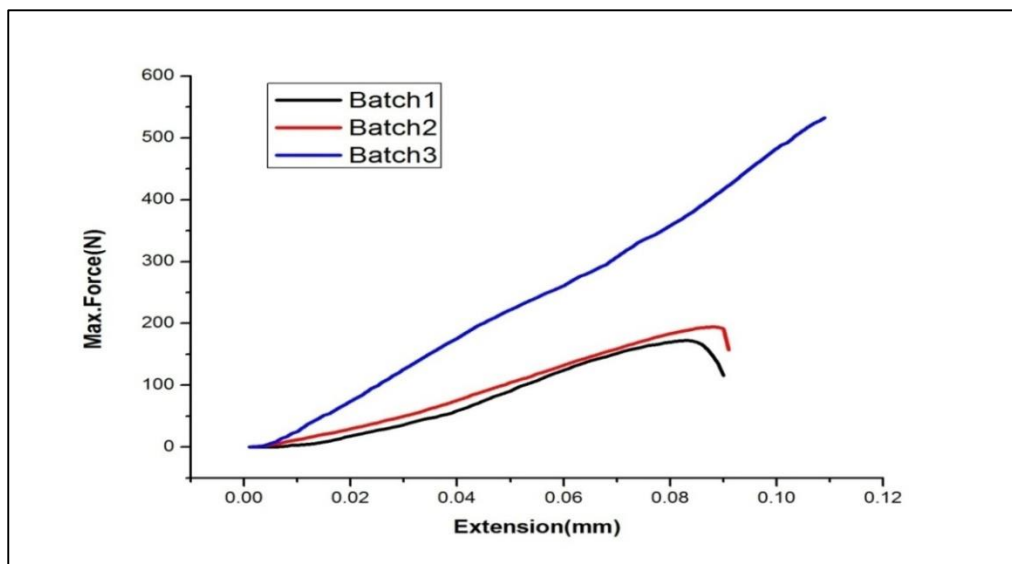


Figure-4.19 three-point bending of glass-ceramics obtained from Batch1, Batch2 and Batch3

4.9 Dilatometer test of glass ceramic:

Table 4.4 Thermal expansion of glass ceramics

	Thermal expansion co-efficient(20-400°C) (/°C)	Thermal expansion co-efficient(400-900°C) (/°C)
Batch1	7.303×10^{-6}	9.491×10^{-6}
Batch2	5.941×10^{-6}	9.54×10^{-6}
Batch3	7.444×10^{-6}	10.118×10^{-6}

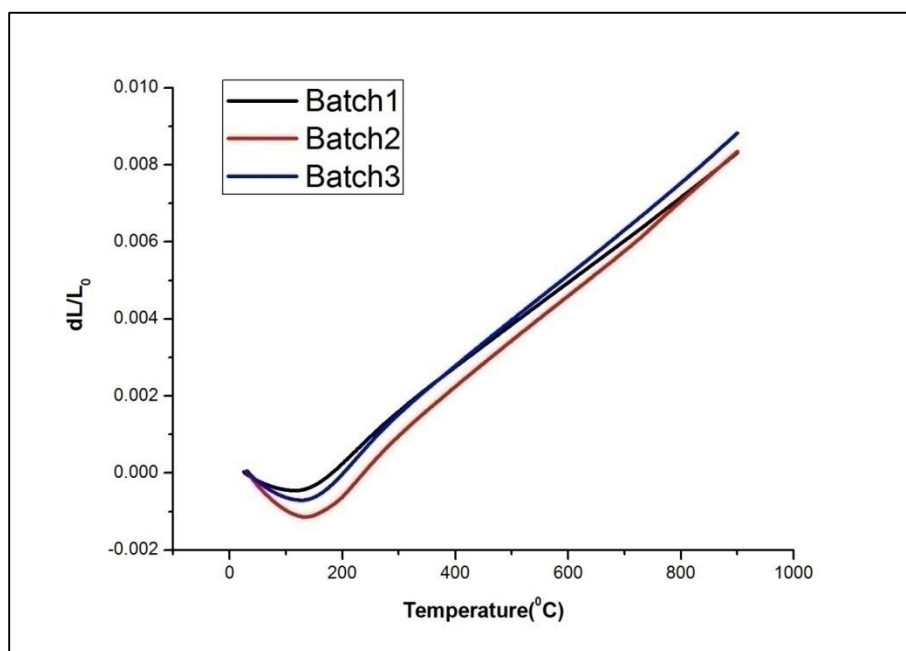


Fig. 4.20 thermal expansion behavior of glass-ceramic obtained from Batch1, Batch2 and Batch3 heat-treated at 900°C

Thermal expansion co-efficient of Batch3 is $7.444 \times 10^{-6}/^{\circ}\text{C}$ in the range of 20-400°C. So it can be utilized in cook-top applications. As there is high alumina substance show in glass ceramic phase in this manner, it indicates less thermal expansion coefficient. The alumina offers high viscosity in glass network at low temperature. So on rising the temperature, the alumina phases can't go inside the free volume. Also, silica phase present inside the glass network gives low thermal expansion co-efficient. The thermal expansion coefficient of the glass ceramic shows an average

rate of $7.444 \times 10^{-6}/^{\circ}\text{C}$ (30–400°C) which is similar the value of Diopside phase. This outcome has been supported by the XRD analysis.

4.10 Compressive strength of glass ceramics:

Table 4.5 Compressive strength of glass ceramics

CCS(MPa)	900°C	1000°C	1100°C
Batch1	102	102	66
Batch2	110.8	128.2	120.1
Batch3	132	139.8	136.1

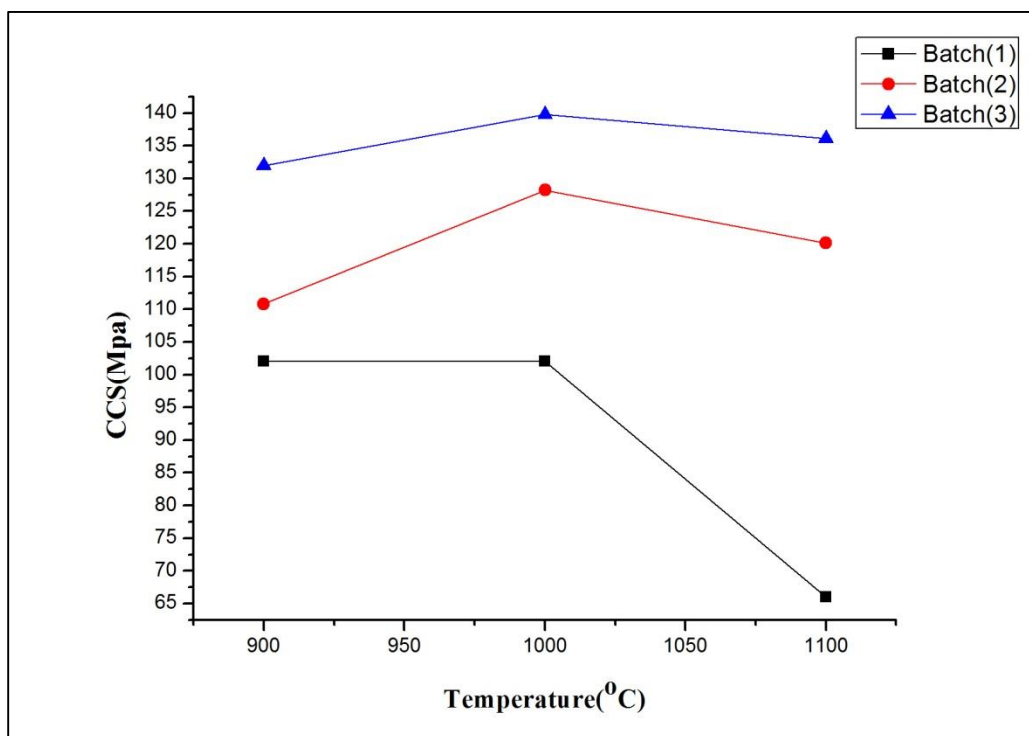


Fig. 4.21 CCS vs. Temperature

As indicated in Fig.4.17 CCS quality increments with increment the temperature in light of the fact that crystalline structure increments with rising the temperature. At 900°C the melting is minimum; subsequently on cooling the crystallization is not noteworthy. Since the glass ceramic arrangement is insignificant, the strength is low for this situation. At 1000°C, the strength is highest

as the crystalline phase formation is the highest here, which is supported by XRD and Density results analysis. At 1100°C, the quality drops because of the dissolving of crystalline phases, i.e. crystallization decreases. The crystallization decreases after 1000°C, which leads to decreases in Compressive strength. The Compressive strength may be decreases after 1000°C due to the micro-cracks inside the glass ceramic network. Density test results also support that after 1000°C density decreases due to more grain growth.

With increases the amount of TiO_2 , Compressive strength also increases due to the higher crystallization with comparison to without TiO_2 system. Because Ti^{4+} Takes the place of Si^{4+} destinations in the glass network presents a Ti-O bond that is weaker than the Si-O bond. These prompts enhance the batch melting and crystallization ability of the glass. Also, FESEM supports that higher crystallization present in TiO_2 system, whereas lower crystallization is present in without TiO_2 system.

CHAPTER: 5

CONCLUSION

5. Conclusion

- The melting temperature for glass-ceramic composition was found to be 1400°C with a soaking time of 1 hour.
- The crystallization is effective after heat treatment above 800°C. The main crystalline phase is Diopside and along with this, a few percentage of gehlenite was found. The maximum crystallization was found at 1000°C. With increasing temperature above 1000°C, crystals dissolve back into the glass.
- Both nucleation and crystallization are increased with increase in temperature. A comparison between Batch2 and Batch3 based glass-ceramics proved this fact. Crystallization temperature is less in glass-ceramic having 5 % TiO₂. Crystallization rate is high with increasing amount of TiO₂.
- The density of glass-ceramics increases with increase in temperature and addition of TiO₂ till 1000°C. After 1000°C, density decreases.
- Hardness increases with the amount of TiO₂ and maximum value found at 900°C. After 900°C, the hardness decreases.
- Flexural strength increases with the increasing TiO₂ content.
- Compressive strength (CCS) increases with temperature and amount of TiO₂ till 1000°C. After 1000°C, CCS value decreases.
- This glass-ceramics showed lower thermal expansion co-efficient. Thermal expansion co-efficient= $7.444 \times 10^{-6}/^{\circ}\text{C}$ in the range of 400°C. So, it can be used as a cook-top application.
- The Final glass ceramic has mechanical properties suitable for application in load-bearing architectural systems.

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